

## Concerning the white paint employed for decorating the pottery of Vădastra II phase at Vădastra

*by Gh. Gâță and Corneliu N. Mateescu, Bucharest*

*In memoriam  
Em. Protopopescu-Pake*

The new archaeological excavations carried out between 1946 and 1974 at Vădastra (fig. 1) on the Măgura Fetelor and Dealul Cișmelei sites have brought to light – from the Vădastra I and Vădastra II strata (Middle Neolithic)<sup>1</sup> – a rich harvest of decorated earthenware<sup>2</sup> (fig. 2 – 3).

One of the major problems that arose from the very beginning of the excavations was that of the origin and of the importance of the white paint used for decorating the earthenware in the Vădastra I and Vădastra II phases (5<sup>th</sup> millenium B. C.).

### Analysed materials

The whitening used in decorating occurs under three aspects: incrustations, granules, and coatings. Incrustations appear as a compact paste of white material filling the incisions of the decorative design; granules are implanted in the walls of the vases, while white coatings make up the ornamental motifs covering part of the surface of the object.

The samples of whitening were collected from a large number of pieces of pottery belonging to the Vădastra culture which occurs at Vădastra, Crușovu<sup>3</sup>, Hotărâni<sup>4</sup>, Ipotești<sup>5</sup>, Celeiu<sup>6</sup>, and Cîrcea<sup>7</sup>. Were also analysed several samples of whitening from pottery of other cultures, either contemporary or not far

<sup>1</sup> EM. PROTOPOPESCU – PAKE, CORNELIU N. MATEESCU et AL. V. GROSSU, Formation des couches de civilisation de la station de Vădastra en rapport avec le sol, la faune malacologique et le climat. *Quartär* 20, 1969, 139 – 141, 147 – 148, 161 – 162.

<sup>2</sup> C. N. MATEESCOU, La plus ancienne phase de la civilisation de Vădastra, Vădastra I, à la lumière des nouvelles fouilles de Vădastra. *Bericht über den V. Internationalen Kongreß für Vor- und Frühgeschichte Hamburg 1958*, Berlin 1961, 533 – 534; idem, Contribution à l'étude de la civilisation de Vădastra: Phase Vădastra II (d'après les nouvelles fouilles de Vădastra). *Atti del VI Congresso Internazionale delle Scienze Preistoriche e Protostoriche Roma 1962*, II, Roma 1965, 260 – 263.

<sup>3</sup> CORNELIU N. MATEESCU, Săpături arheologice la Crușovu. *Materiale și Cercetări arheologice III*, 1957, 105 – 109.

<sup>4</sup> Surface investigations performed by CORNELIU N. MATEESCU in 1962 and ceramic material kindly placed at the author's disposal for investigation by M. NICA from his own sondations carried out in 1967 and 1969.

<sup>5</sup> Surface investigations performed by CORNELIU N. MATEESCU in 1961.

<sup>6</sup> Surface investigations performed by CORNELIU N. MATEESCU in 1946 and pottery sherds offered for study by EXPECTATUS BUJOR from his excavations of 1962.

<sup>7</sup> Ceramic material offered for study by M. NICA from sondations performed in 1971 – 1975.

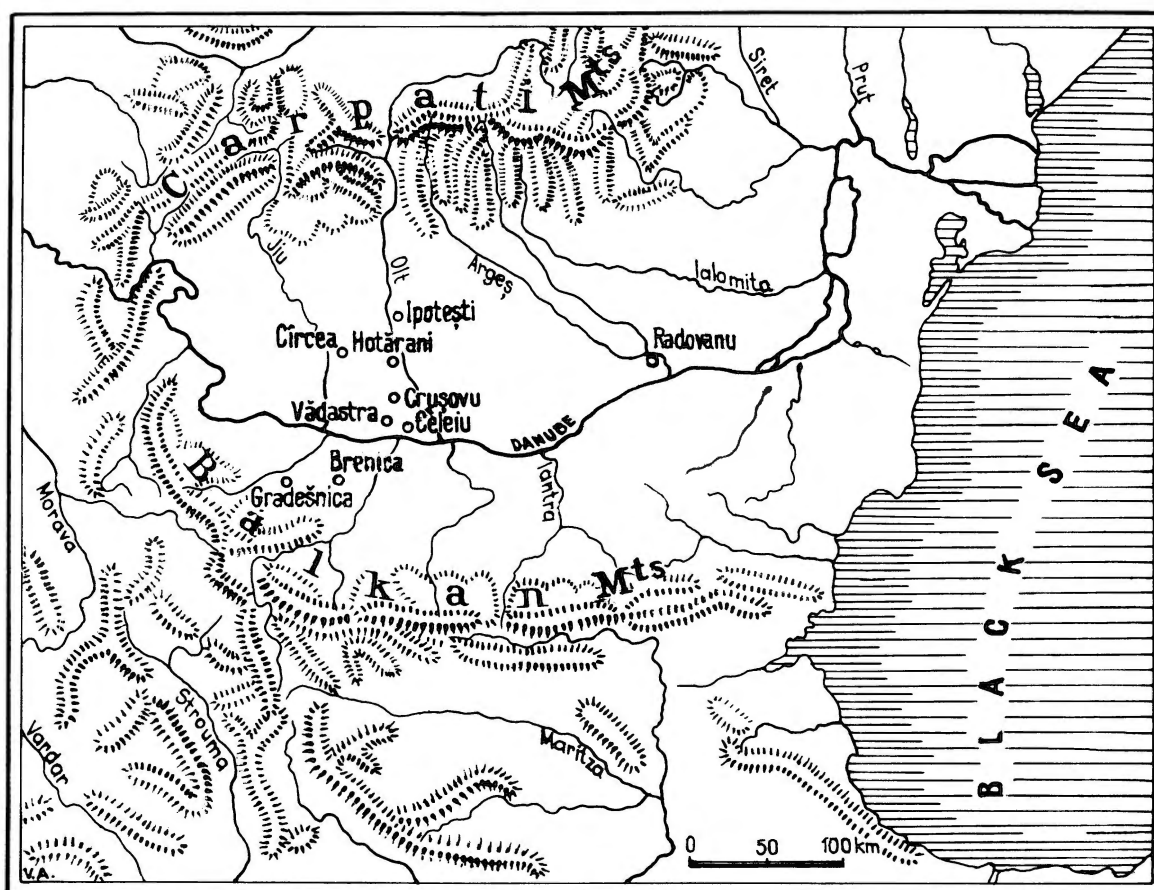


Fig. 1. Map of the Neolithic settlements mentioned in the text.

distant in time: Starčevo-Criș (Vădastra, Cîrcea), Boian (Radovanu, the Spanțov stage)<sup>8</sup> and, from the right bank of the Danube, Gradeșnica<sup>9</sup> and Brenica<sup>10</sup>.

As the ornamental whitening on the Neolithic pottery at Vădastra has the chemical make-up of a marl or marl clay<sup>11</sup>, in order to determine its sources, various samples with similar compositions were analysed, such as carbonate neoformations collected from soils or lithological strata in the perimeter of the Vădastra settlement during the archaeological excavations. Similarly, several samples of whitening found in the layer at Vădastra were analysed, as well as deposits of carbonates on various sherds from Vădastra, Crușovu and Celeiu. Were likewise analysed for the sake of comparison other occurrences of calcium carbonate from various places in southern Oltenia (carbonate concretions, puppets of loess and horizons of carbonate accumulation in the soil). Seeking to assess the distribution of strontium within the sediments of the region, a number of soil samples were analysed, especially from the carbonate accumulation horizon<sup>12</sup>.

<sup>8</sup> Ceramic material offered for study by EUG. COMȘA from his excavations of the last twenty years.

<sup>9</sup> Comparative ceramic material offered by BOGDAN NIKOLOV from excavations performed between 1963 – 1973.

<sup>10</sup> Pottery sherds offered for comparison and study by BOGDAN NIKOLOV from his own excavations.

<sup>11</sup> L. B. RUHIN, *Bazele litologice, Știința rocilor sedimentare*. Translation from the Russian second edition 1961, Editura Tehnică, București 1966, 180 – 182.

<sup>12</sup> Besides previous analyses due to EM. PROTOPOESCU – PAKE, a number of 205 analyses (hydrochloric extract) were performed between 1976 – 1985 by chem. eng. GH. GĂȚĂ from the Institute for Soil Science in Bucharest.

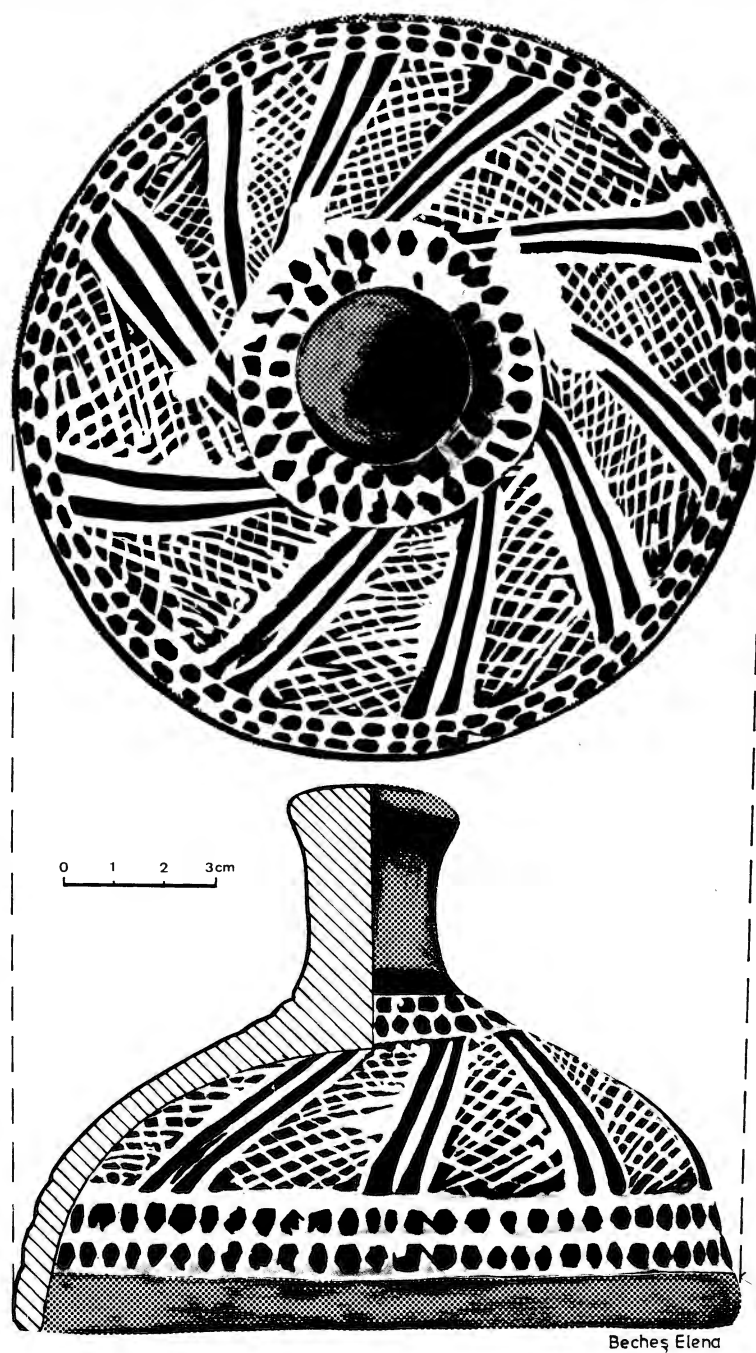
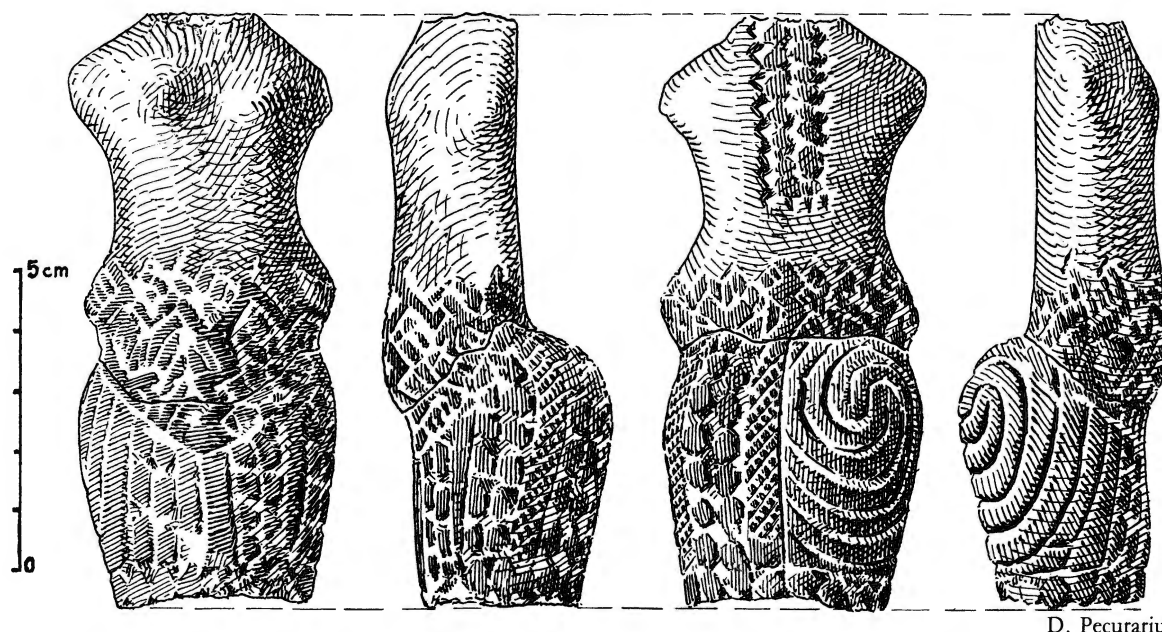


Fig. 2. Vădastra. Lid of a ornamental vessel, decorated by incision and filling with white chalky paste; red colour (= screened area) on rim and shoulder (Vădastra II phase).



D. Pecurariu

Fig. 3. Vădastra. Incomplete female figurine. The creases of the garment can be discerned around the neck (identical with those of present-day smocks worn by Romanian peasant-women); on the back, the plaited hair. Decoration on the figurine represents the skirt (Vădastra II phase).

### Analytical methods

Total chemical composition of samples of whiting was determined by alkaline fusion of the samples<sup>13</sup>. Calcite being the predominant mineralogical component in the white material, preference was given to a method consisting of solubilization of the carbonates in hydrochloric acid (1/3) and titration by atomic absorption of the calcium, magnesium, strontium, and iron in the hydrochloric extract<sup>14</sup>. When the available samples were of only a few milligrams, their smallness called for mineralogic analyses based on absorption in infra-red light<sup>15</sup> or on X-ray diffraction diagrams<sup>16</sup>.

The precision of the analytical methods employed was assessed by comparing the results of duplicate analyses carried out on the mortar-ground and homogenized material of the same samples. The results of more than 10 samples treated by both methods led to the conclusion that determination errors were of less than  $\pm 1.5\%$ .

<sup>13</sup> The chemical analyses were performed according to a variant of the method exposed by M. L. JACKSON, Soil chemical analysis, Constable & Co. Ltd. 1958, 184 – 198.

<sup>14</sup> Mg, Ca, Sr and Fe were determined by atomic absorption spectrophotometry using the resonance lines at 285, 423, 461 and, respectively, 372 m $\mu$  (JOHN A. DEAN, Flame Photometry. New York 1960, 188 – 209).

<sup>15</sup> Calcite, quartz and kaolinite were determined by means of absorption in infra-red light in 1430 cm<sup>-1</sup>, 780 cm<sup>-1</sup> and 3690 cm<sup>-1</sup> bands respectively (GH. GĂȚA, ELENA GĂȚA and C. SCHRAMEK, Determinarea conținutului în carbonat de calciu și carbonat de magneziu în seria izomorfă calcit-dolomit cu ajutorul curbelor de absorbție în infraroșu. Analele Institutului de Cercetări pentru îmbunătățiri funciare și Pedologie, Seria Pedologie 1(35), 1967, 153 – 160.

<sup>16</sup> Micas, kaolinite, quartz, calcite, dolomite and feldspars were determined by means of the intensity of diffraction lines of X-Rays of 10 Å; 7.14 Å; 3.34 Å; 3.032 Å; 2.89 Å and 3.22 Å respectively (G. BROWN, The X-Ray Identification and Crystal Structures of Clay Minerals. London 1961, 467 – 488).

Results. Characterization of the whitening on the earthenware of the Vădastra culture

In order to obtain analytical data concerning the origin of the ornamental whitening, the mineralogical make-up of several samples from Vădastra was determined. The results of analyses by infra-red absorption and by X-ray diffraction show the predominant minerals of ornamental whitening to be calcite and quartz; subordinately, appear clay minerals (illite and kaolinite), feldspars and oxides of iron, manganese and aluminium. Total chemical analyses corroborate the mineralogic composition by showing high contents in CaO (4.5 – 55 %), CO<sub>2</sub> (3.5 – 42 %) and SiO<sub>2</sub> (4 – 88 %).

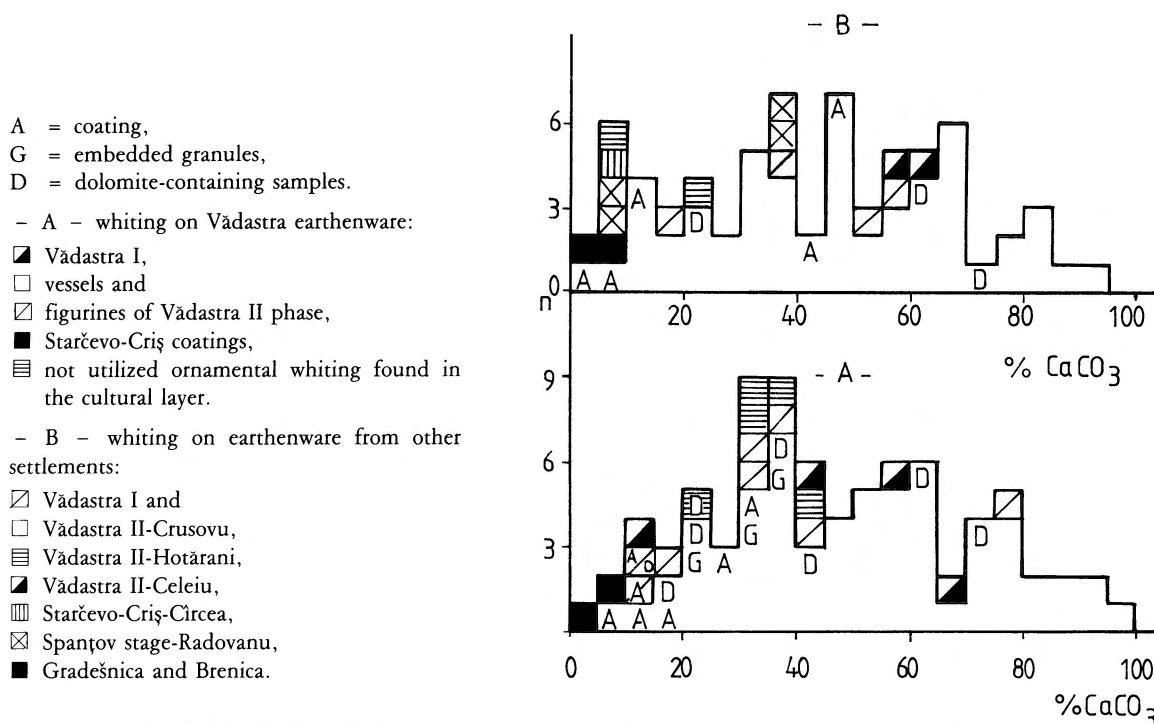


Fig. 4. Distribution of calcium carbonate in the ornamental whitening on Neolithic earthenware.

The concentrations of calcium carbonate in the analysed samples of whitening cover a wide range from 4.3 – 97.2 % (fig. 4-A-). On the whole, the distribution of the samples of whitening from Vădastra is asymmetrical unimodal, with a flattened out maximum of frequency in the 30 – 40 % calcium carbonate range. This asymmetry seems to be due, at least partly, to the position in the histogram of the applications of whitening occurring in the region of low carbonate contents. The low percentage of calcium carbonate in most applications suggests an intrusion of ceramic material from the walls of the clay objects in the white coating.

A detailed analysis of the carbonate distribution show the samples of whitening clustered in three regions of the histogram: under 30 % CaCO<sub>3</sub>, in the 30 – 65 % CaCO<sub>3</sub> range, and over 65 % CaCO<sub>3</sub>. The first region contains 23 % of the samples, namely: white coating from a vessel belonging to the Starčevo-Criș culture, a vessel of the Vădastra I phase, four vessels and a figurine of the Vădastra II phase; calcareous granules taken from a Vădastra II vessel; white incrustations from several pieces of pottery of the same phase.

The second region, with 30 – 65 %  $\text{CaCO}_3$  in the ornamental whitening of Vădastra I and II pottery phases and Vădastra II figurines, includes 56 % of the samples. The third region contains 21 % of the analysed samples: whitening from a Vădastra I vessel, from one figurine and several Vădastra II vessels. The repartition over the entire range of concentrations of the material collected from coatings and fillings of either figurines or vessels shows that the Middle Neolithic pottery at Vădastra made no distinction between the white materials intended for figurines or for pottery. The whitening from the Vădastra I pottery consistently falls between 14.3 – 67.2 %  $\text{CaCO}_3$ , an indication of *continuity in the use of the sources of white material*.

Some of the whitening incrustations on Vădastra earthenware contain between 3 – 9.5 % dolomite. This type of whitening, with 10.4 – 72.3 %  $\text{CaCO}_3$  is not frequent in the incrustations of the analysed pieces and was found in the ornamental whitening of one figurine and of several vessels of the Vădastra II phase. Among the samples of whitening prepared for decorating but unused by the craftsmen potters, only one had 5.7 % dolomite.

The distribution of calcium carbonate in the ornamental whitening of the pottery of other previously mentioned neolithic settlements show a more marked dispersion in the samples containing between 4.6 and 91.3 %  $\text{CaCO}_3$  (fig. 4-B-). The three regions demarcated by the 30 % and 70 %  $\text{CaCO}_3$  limits are readily discernible in the histogram. Besides the coatings and incrustations of vessels of the Vădastra I and II phases at Crușovu, in the first region appear white coatings of vessels from Gradeșnica and Brenica, and samples of pottery of the Starčevo-Criș culture represented at Cîrcea. Also, appear of the pottery of the Vădastra II phase from Hotărani, and of the pottery of the Boian culture, Spanțov stage from Radovanu. In the other two areas appear, together with white of the pottery of Vădastra I and II from Crușovu,

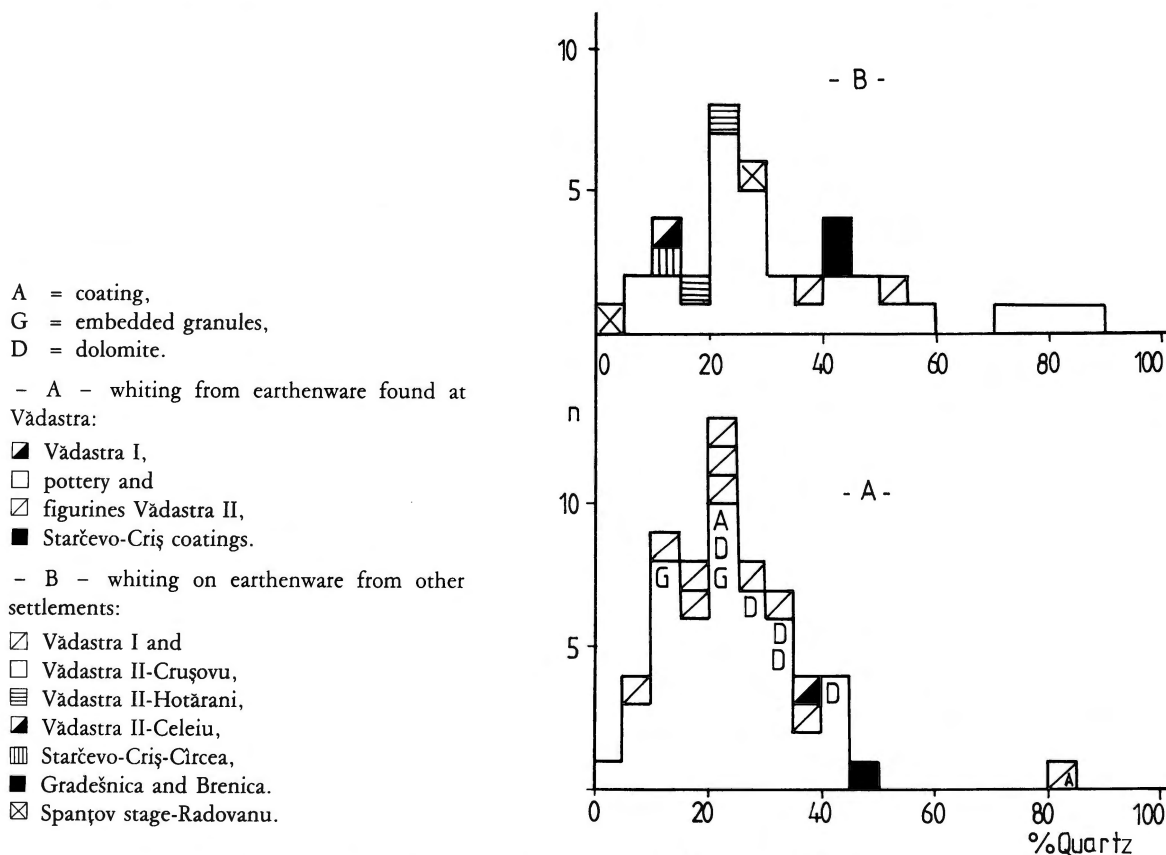


Fig. 5. Distribution of quartz in the ornamental whitening on Neolithic earthenware.

whiting from vessels of the Vădastra II phase at Celeiu, and of the Spanțov stage at Radovanu. Dolomite-containing white decorative pigment was also recognized at Crușovu on three vessels of the Vădastra II phase, in samples with 21.4 – 63.9 – 71.3 %  $\text{CaCO}_3$ .

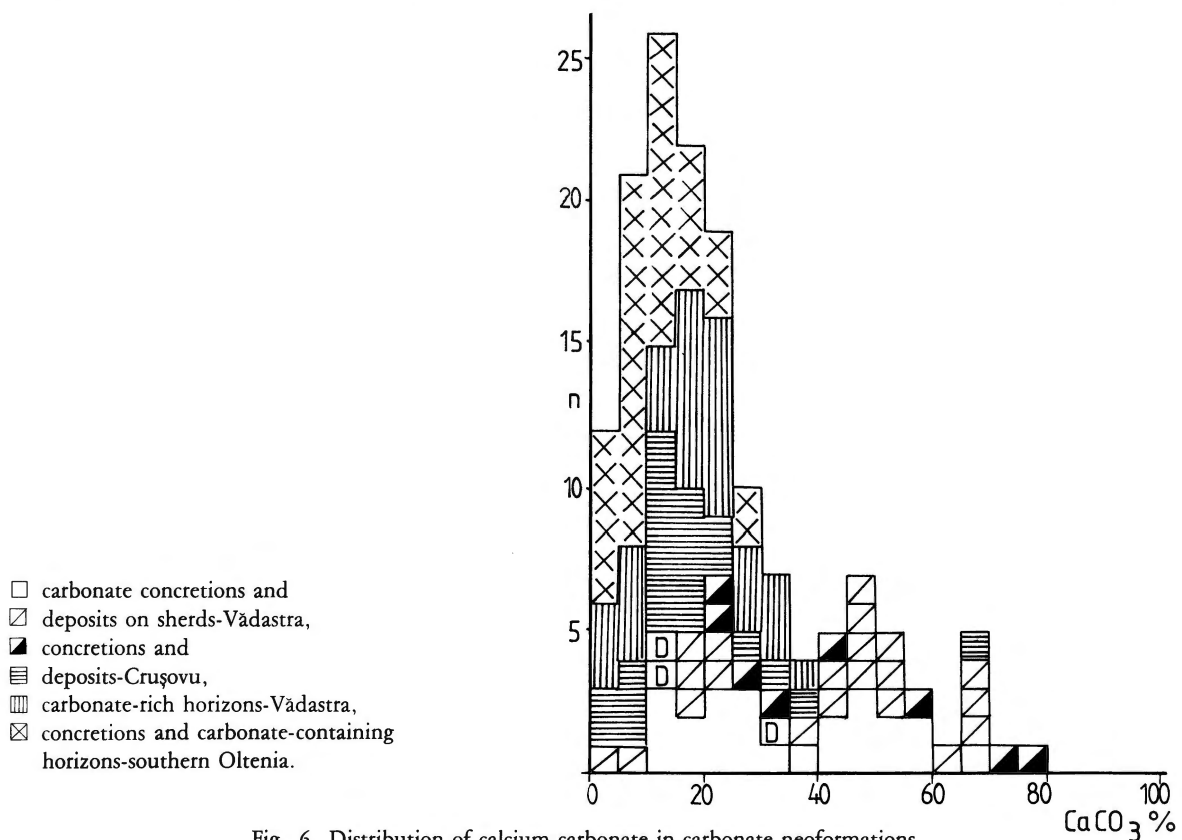
The concentration of quartz in the ornamental whiting on earthenware from Vădastra ranges between 3.4 and 54.2 %  $\text{SiO}_2$ . Exceptionally, outside of the group of distribution appears a sample of the white coating of a figurine of Vădastra II phase, with 82.5 %  $\text{SiO}_2$  (fig. 5-A-). The distribution of quartz in the analysed samples is unimodal asymmetrically with a marked peak between 20 and 25 %  $\text{SiO}_2$ .

The samples of whiting from both phases of Vădastra culture and those belonging to the Starčevo-Criș culture at Vădastra formed a single group of distribution and give evidence of the continuity in the utilization of the same sources of supply throughout the Middle Neolithic at Vădastra.

Compared with the distribution of quartz in the ornamental whiting of the pottery found at Vădastra, the unimodal asymmetrically distribution of quartz in the whiting on earthenware of other Middle Neolithic settlements displays a wider range of concentration (3.8 – 80.6 %  $\text{SiO}_2$ ) but the same maximum of frequency (fig. 5-B-). The coincidence of the two frequency highs shows that all the samples of whiting belong to the same group of distribution and attests that the same type of sources were used for ornamental whiting in the Middle Neolithic settlements of the Lower Danube.

The composition of the white, with variations in wide intervals of concentrations of the calcium carbonate and quartz, as well as the aspect of the white granules embedded in the walls of the pieces of pottery, shows that a composition similar to that of marl clays and of quartz-rich marls to the type of carbonate accumulations in soils and lithological formations with a middling and coarse texture.

The carbonate concretions and deposits on sherds of the pottery in the perimeter of the Vădastra and Crușovu settlements, and the neoformations occurring in southern Oltenia soils exhibit carbonate and



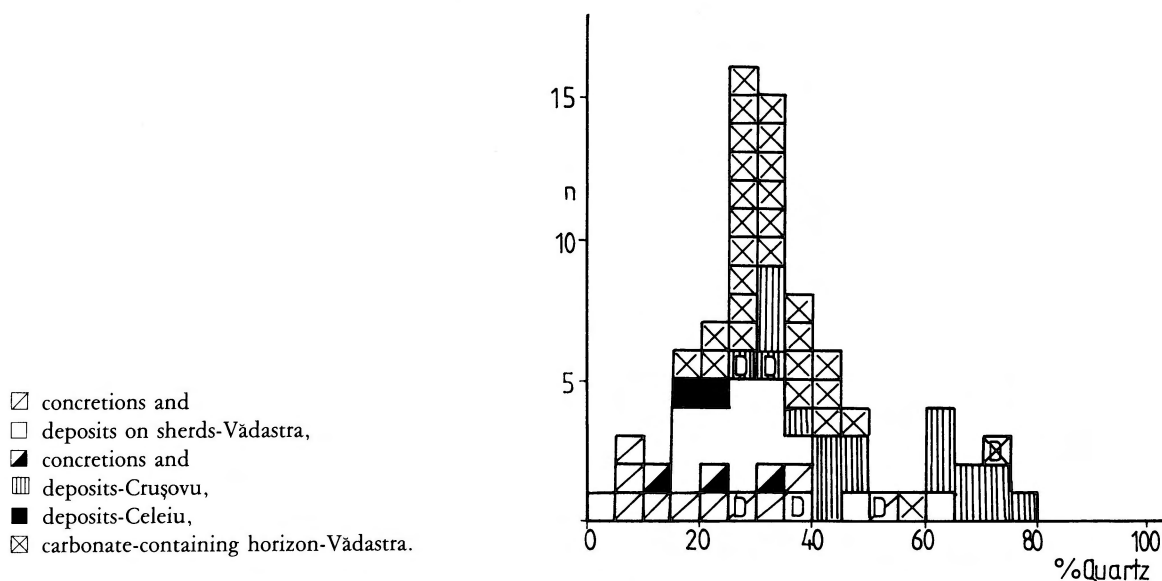


Fig. 7. Distribution of quartz in the carbonate neoformations (D = dolomite-containing samples).

quartz distributions similar to those of the ornamental whitening samples. The maximum frequency in the unimodal asymmetrically distribution of carbonates (fig. 6) occurs of lower values (10 – 15 %  $\text{CaCO}_3$ ) owing to inclusion in the histogram of the carbonate accumulations in the soils. Should we reconsider only the concretionary forms together with the carbonate deposits on the archaeological peaces, three regions of occurrence can be noted, limited by 30 and 65 %  $\text{CaCO}_3$  values, suggesting the use of local neoformations for the ornamental whitening. The distribution of quartz (fig. 7) is unimodal with a marked asymmetry and a maximum frequency at higher quartz concentrations (25 – 35 %  $\text{SiO}_2$ ) than in the ornamental whitening.

The lower calcium carbonate and higher quartz contents in carbonate neoformations as compared with the corresponding figures for ornamental whitening denote a selection of processing of these materials aiming to a concentration of carbonates in the ornamental whitening together with elimination of quartz. The analyses performed pointed to the carbonate neoformations in the soils or lithological formations as the source of white pigment.

#### Comparison of white pigment samples with carbonate neoformations

The mineralogical analysis of white pigment samples taken from the investigated earthenware and that of carbonate-containing lithological samples make evident that the predominant minerals in both categories of materials are calcite and quartz. The variation of the amount of calcite in the samples related to their quartz content (fig. 8 and 9) shows that the representative points in such a diagram are grouped in a band-like area containing both the samples of whitening taken from pottery and figurines from Vădastra, Crușovu and other Neolithic sites, and the carbonate-containing lithologic samples from Vădastra and Crușovu. The concomitant occurrence in the same area of the whitening samples and of the carbonate neoformations points to the fact that these lithological formations might well be the sources of the ornamental whitening applied to neolithic pottery. The width of the band containing the representative points, which is in fact the measure of the dispersion of the points resulting from the presence of the



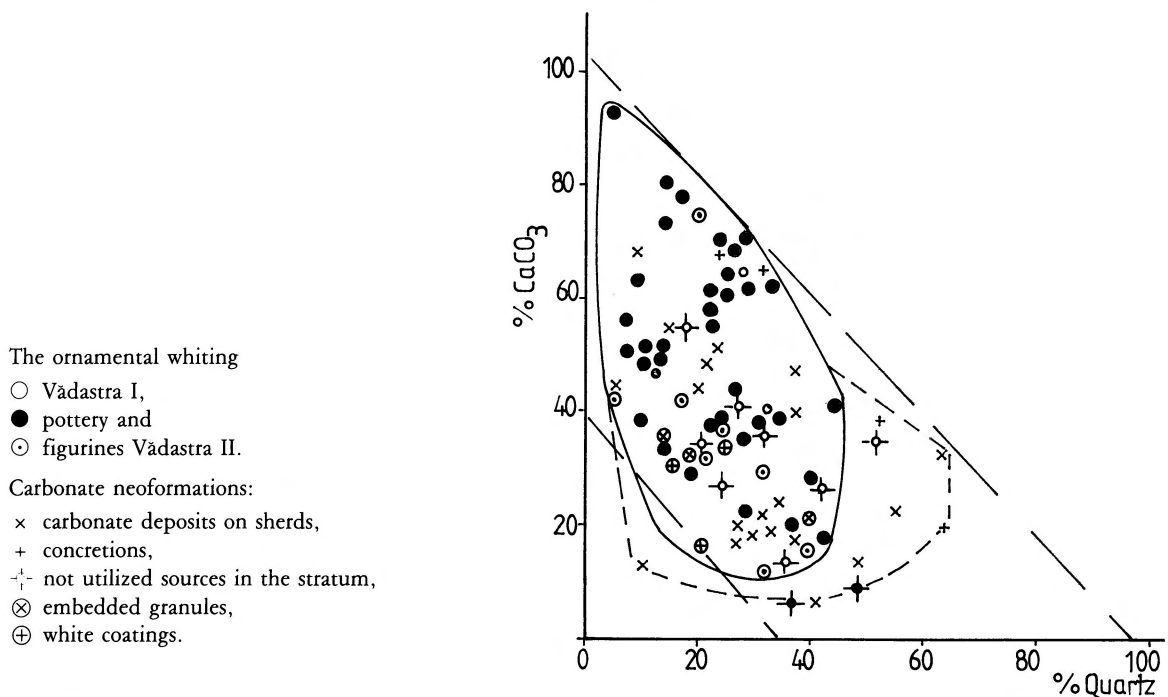


Fig. 8. Distribution of the samples of ornamental whitening and carbonate neoformations from Vădastra.

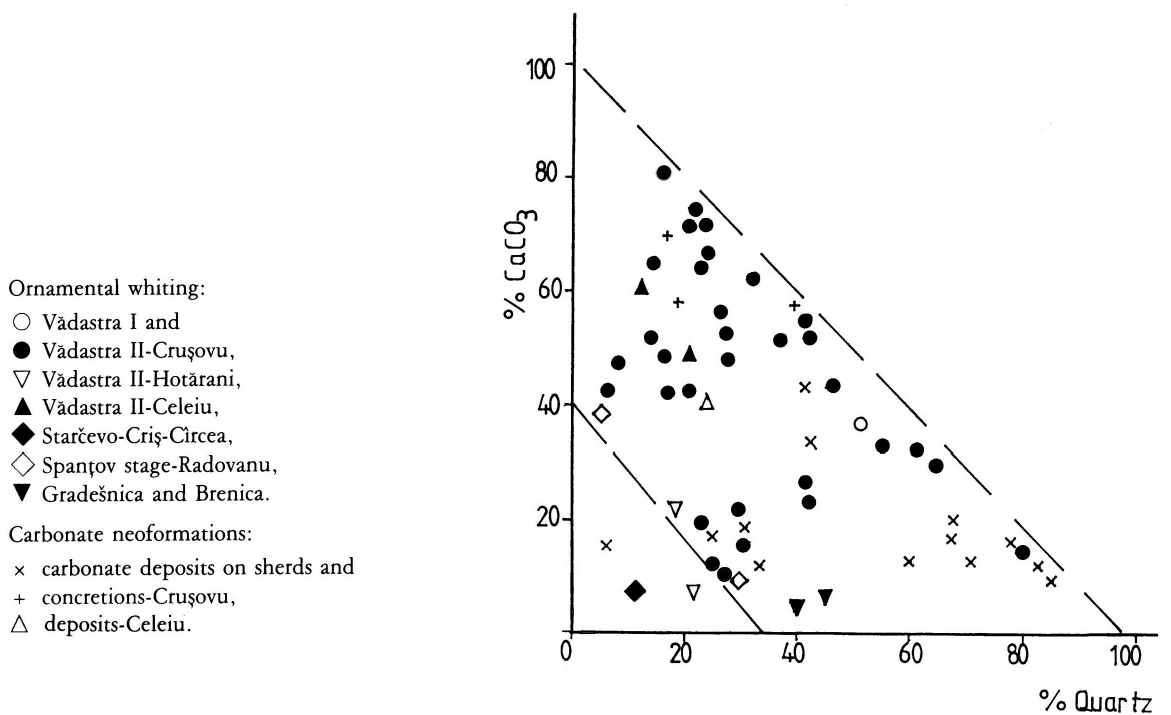


Fig. 9. Distribution of the samples of ornamental whitening and carbonate neoformations in other investigated settlements.

other mineralogic components in the samples, is marked off in the diagram by two nearly parallel dotted lines.

Lying outside the band, nearer the point of origin are whitening samples from Starčevo-Criș culture pottery found in the Vădastra and Cîrcea sites, and whitening from incrustation on a vessel of the Vădastra II phase at Hotărani.

The clustering of most of the analysed samples in the area between the two straight lines emphasize the predominance of the two mineralogic components while also showing that the degree of whiteness remains adequate for the samples to be selected, even with higher concentrations of clay minerals, feldspars etc. with a darkening effect. In the diagram, the dilution of the carbonate with such minerals causes the shifting of a point with a given calcite/quartz ratio in a direction nearly at right angles with the dotted boundary lines.

The common occurrence in the same area of the points pertaining to whitening samples and to neoformations shows the sources of supply to be local and of the type of the neoformations. At the same time, the lack of separation in different parts of the diagram of the points corresponding to figurines or to vessels proves that no selection of white materials was implied for the two categories of pieces in the Vădastra II phase at Vădastra. Moreover, the statistical relations between the carbonate (y) and quartz (x) contents computed for the groups of whitening samples from Vădastra and Crușovu, and for the carbonate neoformations from both sites, are expressed by a pencil of straight lines with negative sub-unity angular coefficients, and whose ordinates at the origin have positive values ranging from 49.31 and 62.47.

Generally speaking, the statistical data show that the choice of materials for ornamental whitening, or the technique of selection used in both settlements, were similar and consisted in improving the carbonate content and eliminating quartz, as indicated by the mean values (Table 1).

Table 1

Statistical equations relative to the comparison of the ornamental whitening with the local carbonate neoformations (y = contents in calcite; x = contents in quartz)

n	Group of samples	Equation	r**	Quartz	Calcite
51	Ornamental whitening (Vădastra)	$y = 60.61 - 0.68x$	0.44***	21.7	44.6
31	Neoformations (Vădastra)	$y = 49.31 - 0.40x$	0.43*	32.6	34.4
34	Ornamental whitening (Crușovu)	$y = 61.52 - 0.51x$	0.42*	31.5	45.5
19	Neoformations (Crușovu)	$y = 56 - 0.61x$	0.69***	50.3	25.2
14	Whitening from other settlements	$y = 43.71 - 0.93x$	0.66*	24.1	20.3

n = number of analysed samples;

r\*\* = coefficient of correlation of the statistical equation;

\* and \*\*\* = mathematical significance of the coefficient of correlation.

The fact that whitening samples from the other neolithic settlements investigated presents an equation of the same type shows that, in the Middle Neolithic, the technique of selecting or preparing the ornamental whitening was the same in all the settlements along the Lower Danube. Moreover, the mean data of the analysed samples of each group make manifest a higher concentration of quartz both in the ornamental whitening and the carbonate neoformations at Crușovu as compared with the corresponding materials at Vădastra.

The results obtained by comparing the samples of whitening from neolithic pottery with the carbonate neoformations in the vicinity of the sites prove that *the sources of material were the local concretionary forms and that the ornamental whitening resulted from the selection or preparation of a material having a higher content of calcite and a lesser one of quartz.*

### Analysis of the extract in hydrochloric acid (1/3)

The analysis of the samples of whitening collected from the Middle Neolithic pottery found at Vădastra and Crușovu as well as of some carbonate neoformations from southern Oltenia shows that the distribution of the solubilized elements is similar for both categories of materials and characteristic for marl clays and marls.

The distribution of calcium is very much alike to that of calcite, having a field of occurrence of 0.9 and 36.7 % calcium and a maximum frequency of the samples between 12 and 14 % calcium. This parallelism between the distributions of calcium and calcite is explained by the total dissolution in the acid of the calcium carbonate, the predominant mineral in the analysed samples. The samples of carbonate neoformations from southern Oltenia are coincident with the samples of whitening and of the carbonate formations of Vădastra and Crușovu in the histogram of calcium repartition, thus attesting that the interval of occurrence is common to all the carbonate formations throughout the sedimentary deposits of southern Oltenia.

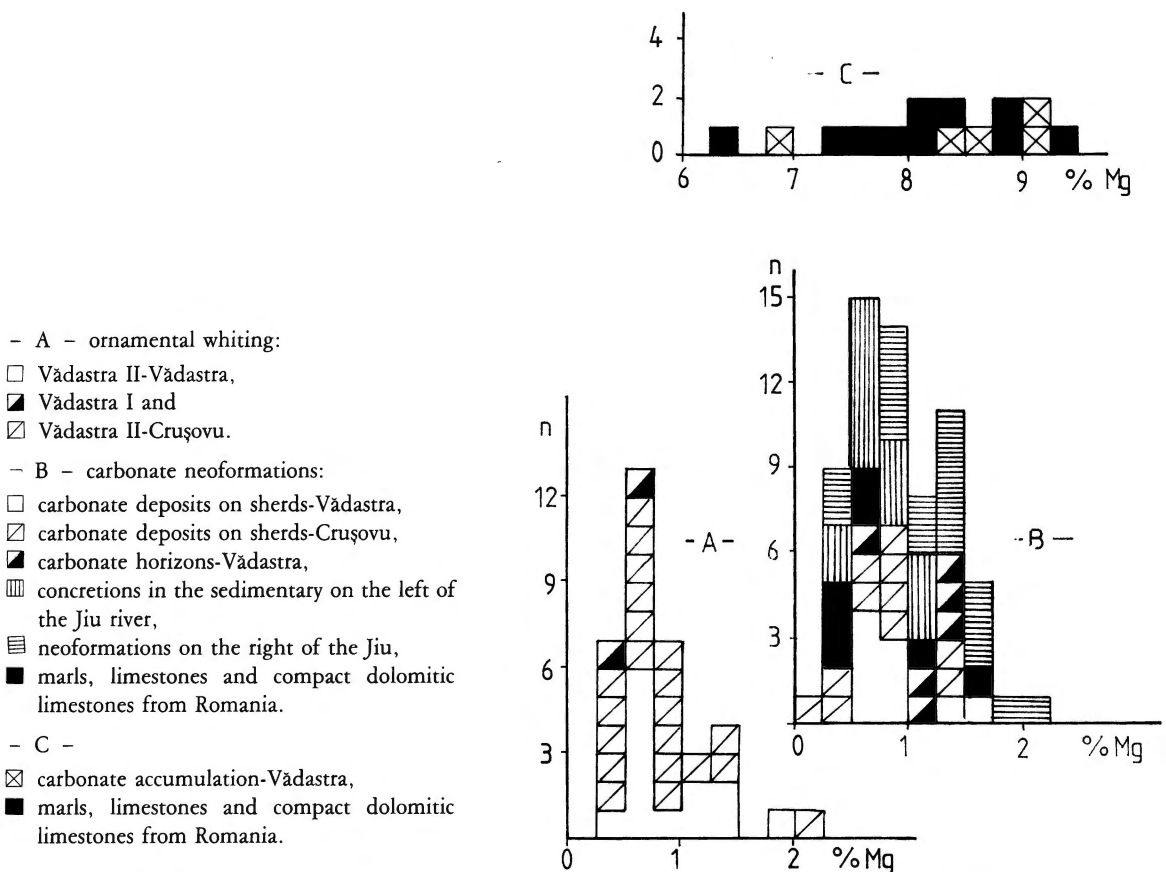


Fig. 10. Distribution of magnesium in the ornamental whitening and in carbonate neoformations.

The distribution of the magnesium found in the ornamental whitening is unimodal asymmetric, with values ranging from 0.26 and 3.15 % Mg. The peak frequency lies in the 0.5 – 0.75 % Mg interval both for the samples from Vădastra and those from Crușovu (fig. 10 -A-). Some of the samples from the continuous concretionary stratum of Vădastra have comparatively large amounts of dolomite and a content of solubilized magnesium of 6.91 and 9.25 %.

Compared with the samples of whitening from the Middle Neolithic earthenware, the carbonate neoformations within the perimeter of the Vădastra and Crușovu settlements have a similar unimodal asymmetric distribution: maximum frequency between 0.5 and 0.75 % Mg (fig. 10 -B-) and the interval of occurrence 0.17 – 2.22 % Mg. The distribution of the samples of concretionary formations from southern Oltenia is similar, but with a flatter maximum between 0.5 – 0.75 % Mg and a wide range of variation (0.17 – 9.23 % Mg), if the dolomite-containing samples are also considered. The position of some geological samples of limestones and compact dolomitic limestones (fig. 10 -C-) shows that they cannot be differentiated from the carbonate neoformations of southern Oltenia.

The distribution of strontium in the ornamental whitening of Vădastra and Crușovu earthenware appears unimodal and slightly asymmetric, ranging from 86 and 957 ppm Sr and a maximum frequency in the 200 – 400 ppm Sr interval (fig. 11 -A-). Comparatively, the distribution of the strontium extracted from neoformations of southern Oltenia is unimodal and markedly asymmetric, with a maximum between 24 – 100 ppm Sr and an interval of occurrence ranging from 24 and 146 ppm Sr (fig. 11 -B-). The repartition of this element sets the whitening used on the Vădastra and Crușovu earthenware together with the neoformations present in the perimeters of these sites and largely separates them from the other

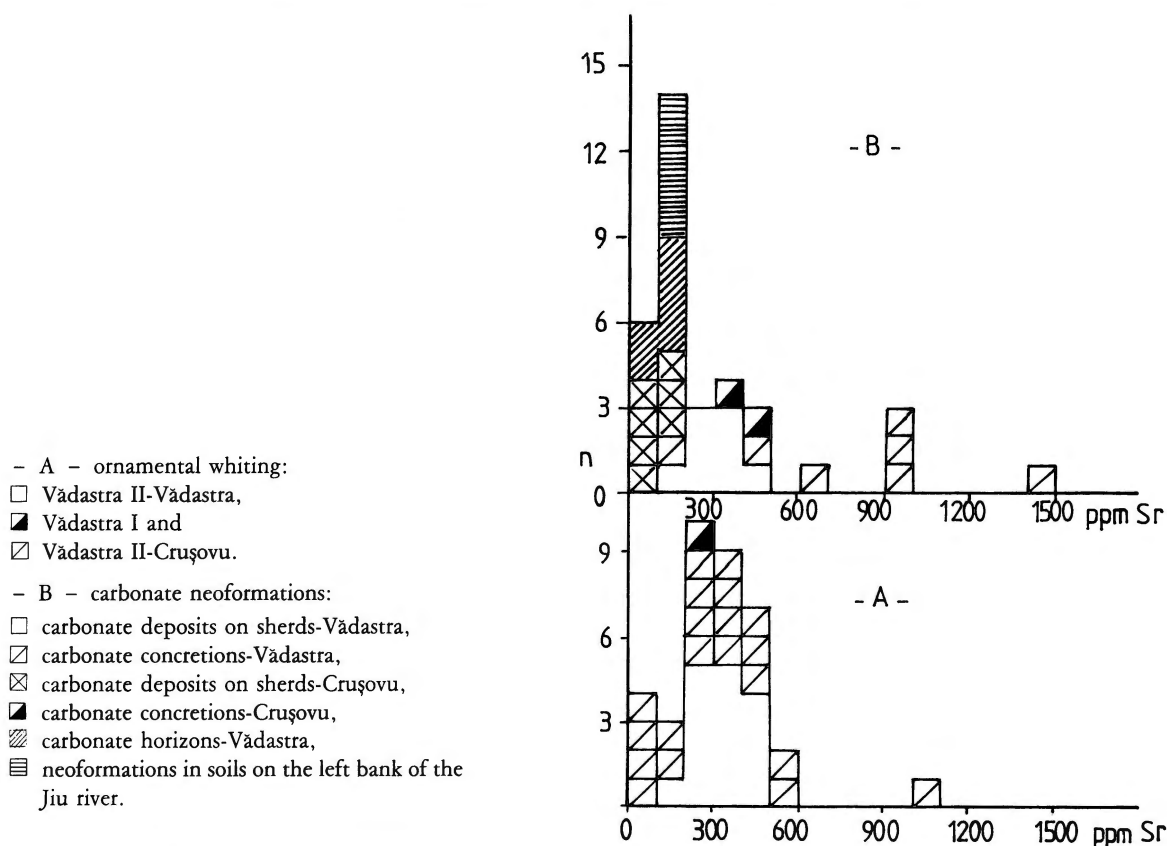


Fig. 11. Distribution of strontium in the ornamental whitening and in the carbonate neoformations.

similar samples from southern Oltenia. Should we consider only the samples taken from the concretionary strata and the carbonate concretions of Vădastra and Crușovu, their distribution is similar to that of ornamental whitening of the earthenware of these two sites.

The concentration of strontium in the analysed samples allows to distinguish the neoformations of Vădastra and Crușovu from the other concretionary formations in southern Oltenia and proves that the carbonate neoformations present within the perimeter of both settlements were the local sources of ornamental whitening.

The iron extracted in hydrochloric acid originates chiefly in the iron oxides and argillaceous minerals present in the analysed samples, its distribution in the whitening being unimodal and asymmetric with a maximum frequency between 0.75 and 1 % Fe and an interval of occurrence ranging from 0.30 – 3.15 % Fe (fig. 12 -A-). The carbonate neoformations in the area of these two sites offers a distribution which is similar to that of the ornamental whitening from Vădastra and Crușovu, while differing from the distribution of the neoformations of southern Oltenia whose maximum lies between 1.75 – 2 % Fe (fig. 12 -B-). As can be seen in fig. 12, the highest frequency of the Vădastra and Crușovu neoformations is removed towards higher values by the other samples from southern Oltenia, which are mostly clustered between 1.5 and 2.5 % Fe.

Analysis of the hydrochloric acid extract shows that with increasing calcium contents in the extracts, i.e. calcite contents in the samples, there is a decrease of solubilized iron, owing probably to the smaller amounts of iron oxides and argillaceous minerals in the samples.

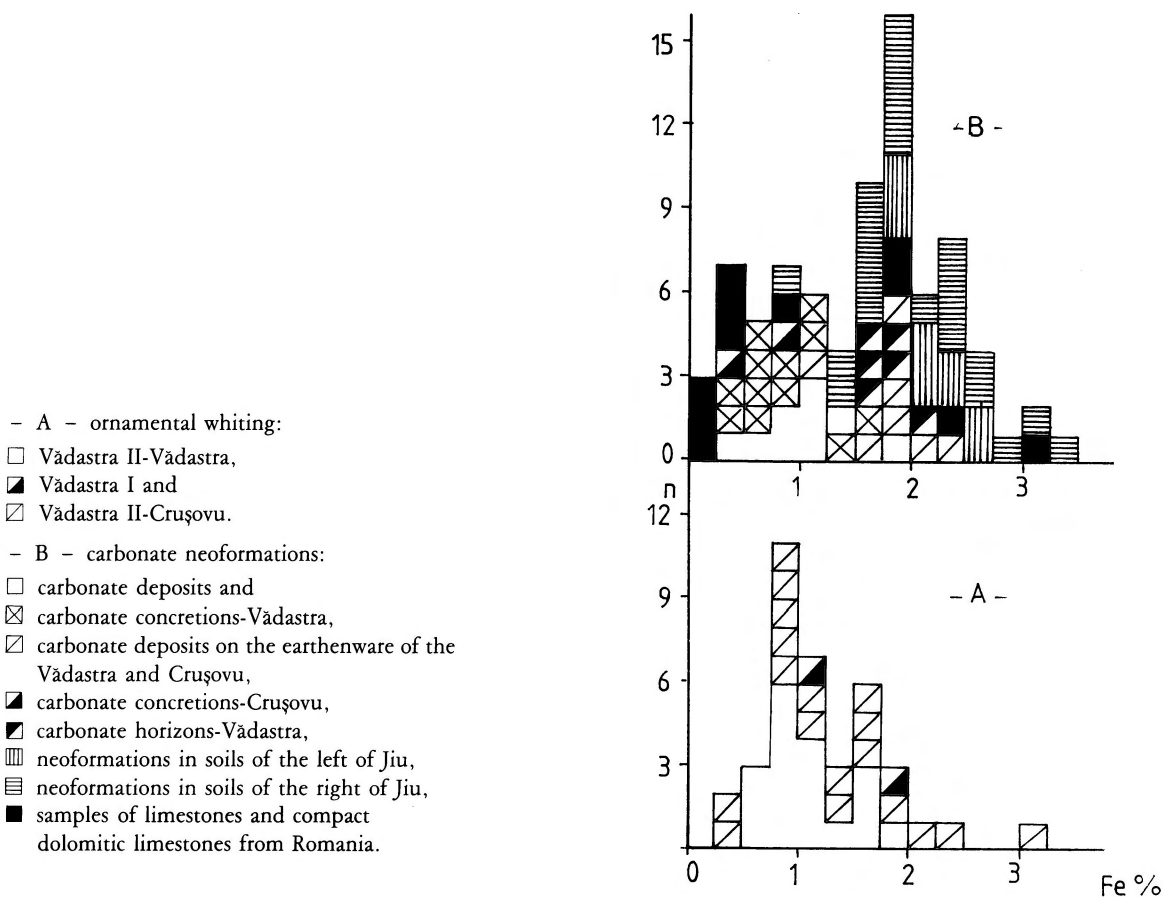


Fig. 12. Distribution of iron in the ornamental whitening and in carbonate neoformations.

The distribution of the extracted magnesium shows no significant differences between the samples of whitening and the carbonate neoformations, as hydrochloric acid solubilizes both the magnesium in the carbonates and that present in the clay minerals and the feldspars in the samples. In this way, there is a compensation between the magnesium solubilized from the silicates and that from the carbonates, resulting in small variations of the magnesium in the extract.

The strontium content in the hydrochloric extract appears as a characteristic of the neoformations at Vădastra and Crușovu as well as of the whitening used in these two locations, setting them apart from other neoformations of southern Oltenia, which have a lesser strontium content.

In conclusion, the results of analysing the obtained hydrochloric acid extracts (1/3) prove this to be valuable for characterizing the samples of whitening from the Middle Neolithic earthenware of the Lower Danube. *The contents in calcium, magnesium, and iron show that the white material is similar to the concretionary materials in the soils and lithologic formations, while the strontium content specifically indicates that the ornamental whitening was obtained from local sources of carbonate neoformations within the perimeter of the settlements or in their close vicinity.*

#### Determination of the sources of ornamental whitening of earthenware of the Vădastra culture

As was already shown, the strontium content in the white paint coincides with that of the carbonate neoformations of Vădastra and Crușovu. The similar chemical properties of calcium and strontium and the small difference in the solubility of the carbonates of these two cations suggest that the two elements taken together might better characterize the investigated samples.

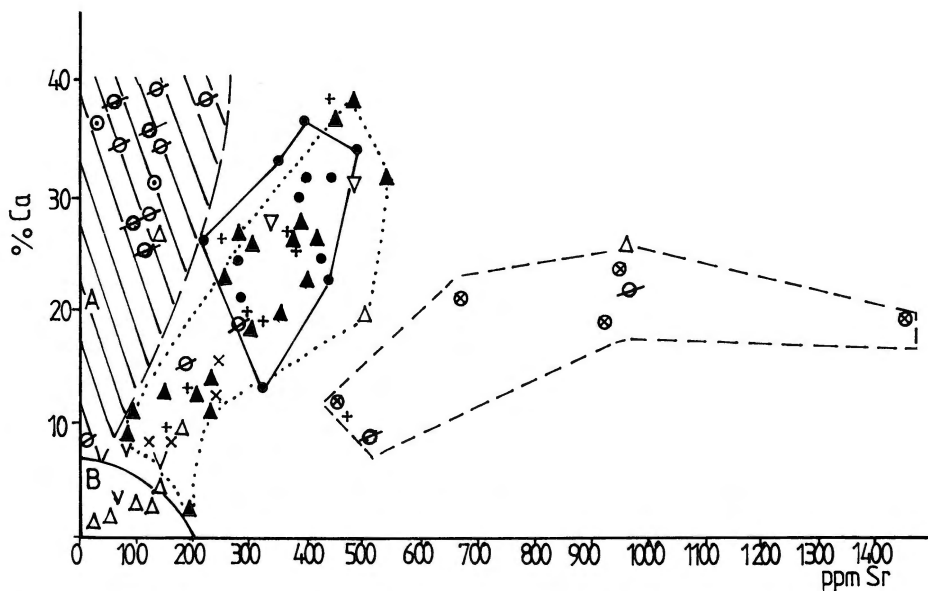


Fig. 13. Distribution of the samples of ornamental whitening of the carbonate neoformations and of some limestones in regard to their contents in calcium and strontium.

Ornamental white: ● Vădastra, ▲ Crușovu. Limestones deposits on sherds: + Vădastra, △ Crușovu. Dolomite-containing concretions: ⊗ Vădastra. Carbonate horizons: ▽ Vădastra, ▽ Crușovu. Neoformations in southern Oltenia: ⊙. Compact limestones: ⊘.

The repartition of the samples according to their calcium and strontium contents (fig. 13) shows that most carbonate-containing lithological formations and soil horizons in southern Oltenia contain less than 100 ppm Sr. Only a few samples collected on the right side of the river Jiu, at Cujmir and Afumați, had between 100 and 215 ppm strontium.

Some of the soils at Vădastra have carbonate-containing horizons with some 60 – 236 ppm Sr. Samples of white pigment taken from pottery of the Vădastra II phase from Vădastra and Crușovu, as well as concretions from the same sites, generally fall in the region with over 10 % Ca and 100 – 450 ppm Sr, thus confirming the utilization of such concretions as sources of ornamental whitening.

The area with more than 550 ppm Sr contains only one whitening sample from Crușovu and five samples of concretionary accumulations from Vădastra; they all contain variable amounts of dolomite and are situated outside the area of ornamental whitening samples.

The calcium-rich compact limestones and carbonate concretions fall within an area lying along the ordinates axis. The area in the vicinity of the origin comprises the representative points of the concretionary formations of southern Oltenia soils.

The region marked by the ornamental whitening from pottery at Vădastra is smaller than that of the carbonate neoformations collected within the settlement and in their vicinity. The field of the white pigment contains only the points corresponding to the carbonate deposits on fragments of pottery, an indication that *the concretionary forms at the level of carbonate accumulation in the soil were the main sources of whitening in the Middle Neolithic at Vădastra.*

At Crușovu, the field defined by the samples of ornamental whitening nearly coincide with that corresponding to the neoformations found within the settlement. The widely greater variations in the composition of the whitening from pottery of the Vădastra II phase found here denote a lesser degree of selection or processing of the raw material, probably owing to large variations in the local concretionary forms or to a more rudimentary processing of the whitening, or even to some of the pieces – or only whitening – being brought from other places.

As results from the Ca-Sr diagram, the contents in these elements clearly distinguish most of the samples of whitening and of concretionary materials from Vădastra and Crușovu from concretionary forms occurring in other places in southern Oltenia. This is a strong argument in favour of the assumption that carbonate neoformations from the sites of these settlements have been used as local sources of whitening during the Middle Neolithic period on the Lower Danube.

The distribution of strontium providing the best means of separating the ornamental whitening and the carbonate neoformations occurring within the neolithic settlements from the concretionary formations in other places of southern Oltenia, the variation of this cation was studied in relation to the Ca/Sr ratio in order to demonstrate that the whitening came from local concretionary carbonate sources.

As in the former diagram, the points corresponding to the ornamental whitening on the Vădastra were of the Vădastra II phase are grouped within a restricted field, smaller than that of the carbonate neoformations occurring in the site, and bear testimony to a careful selection or processing of the concretions is making the ornamental whitening (fig. 14). In this case also, the concretions in the carbonate accumulation horizons in the soil, of the type of those cropping out in the bank of the Obîrșia brook at the foot of Dealul Cișmelei, predominantly lie within the field of the ornamental whitening. The samples of dolomite containing whitening and with more than 550 ppm strontium from the lithological formation present in the perimeter of the settlement were probably not used as sources of whitening, owing to the presence of coarse quartz and the lesser accessibility of the concretionary layer.

The samples of whitening from Crușovu earthenware define a wider area, with a lower Ca/Sr ratio. Excepting the carbonate deposits on some sherds, which contain less than 120 ppm Sr, the area of ornamental whitening in the diagram coincides with that of the local concretionary formations, pointing to the carbonate neoformations within the perimeter of the settlement as its sources. Carbonate neoforma-

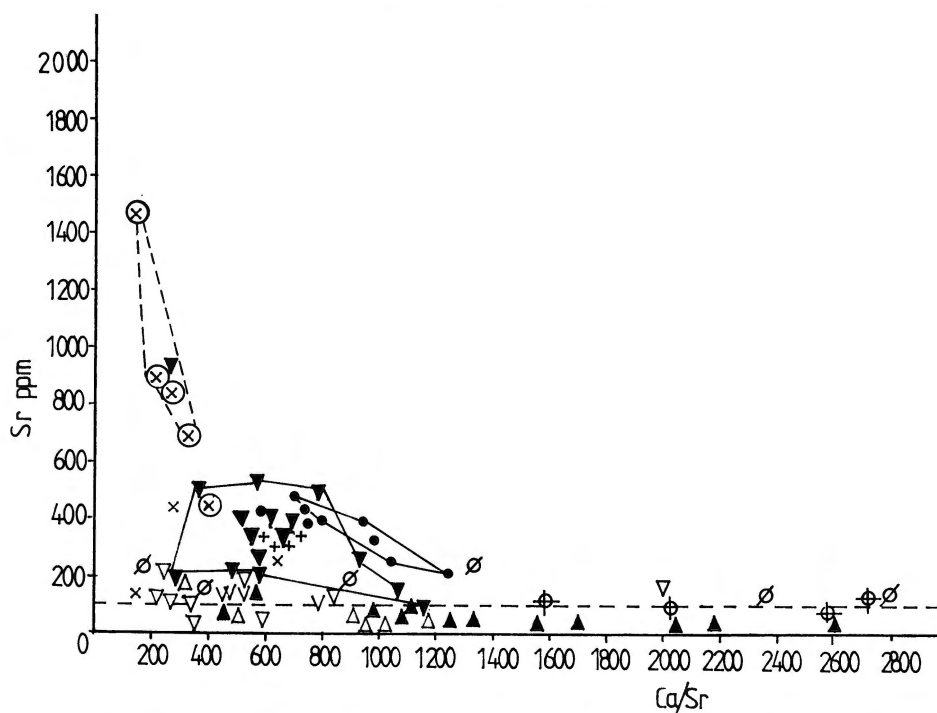


Fig. 14. Distribution of the samples of ornamental whitening, of carbonate neoformations and of some limestones in regard to their contents in strontium and to the Ca/Sr ratio.

Ornamental whitening: ● Vădastra, ▼ Crușovu. Carbonate deposits on sherds: + Vădastra, △ Crușovu. Dolomite-containing concretionary strata: ⊗ Vădastra. Carbonate horizons: ▽ Vădastra, ▲ Crușovu. Neoformations from southern Oltenia: ∅.

tions from other places in southern Oltenia and the Banat are generally grouped along the abscissa limited by the 100 ppm Sr ordinate.

A representation of the strontium content plotted against the Ca/Fe ratio (fig. 15), which approximates the intensity of whiteness also shows a clear separation between neoformations from other localities, on the one hand, and the ornamental whitening and local concretionary formations of the Vădastra and Crușovu sites on the other. The area defined by the whitening samples from the earthenware found at Vădastra is smaller than that resulting from the neoformations of the same site, while at Crușovu the two areas are nearly identical; only one sample of whitening from a Crușovu vessel of the Vădastra II phase and containing 7.8 % dolomite, appears apart from the group of the other samples of whitening. Concretionary aggregates from the lithologic formations within the settlement at Vădastra form a separate area in which, significantly, there are no points corresponding to the ornamental whitening of Vădastra, an indication that these materials were avoid as ornamental whitening.

Carbonate concretions from other points in southern Oltenia compactly cover region A near the origin (fig. 15), while other carbonate concretions from the Banat and Wallachia soils appear in the B area along the absciss. In zone C, along the ordinate, are groupes samples of dolomite and dolomitic limestones from the Dobrudja.

The repartition of the samples analysed with respect to their strontium content in correlation with calcium, to the Ca/Sr and Ca/Fe ratios shows that *the sources of the ornamental whitening for the earthenware at Vădastra and Crușovu are the local carbonate neoformations at the carbonate accumulation level in the soil.* These very much resemble the whitening material cropping out in the bank of the



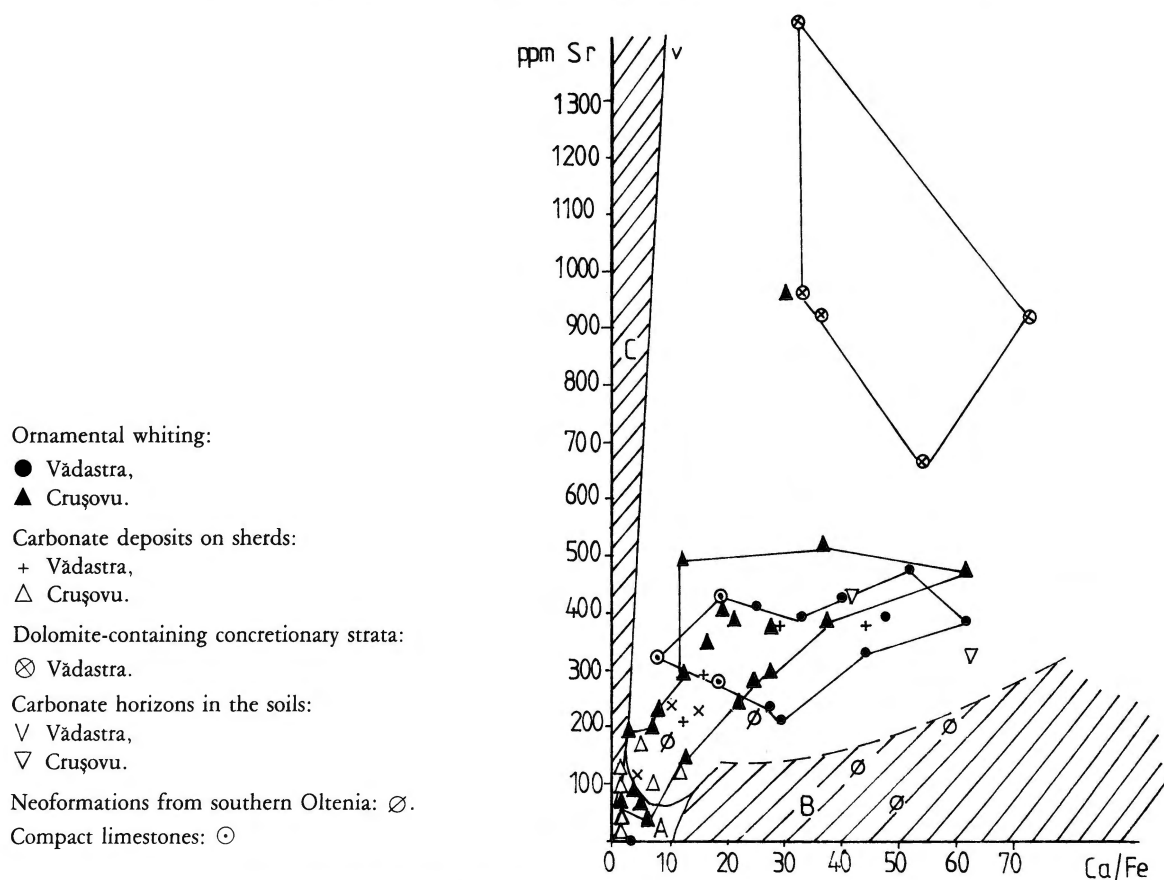


Fig. 15. Distribution of the samples of whitening, of the limestone neoformations and of some limestones to their contents in strontium and the Ca/Fe ratio.

Obîrșia brook, at the foot of Dealul Cișmelei hill. The concretionary carbonate layer inside the perimeter of the settlement, with over 450 ppm Sr and 10 % dolomite, stands apart as a group of white materials not used for ornamental whitening at Vădastra.

In all the diagrams shown here, the area covered by the samples of whitening from Vădastra is smaller than that of the neoformations within the perimeter of the settlement and its immediate vicinity, denoting a selection and processing of the concretionary material in order to obtain the white pigment. At Crușovu, the sorting and processing of the concretionary materials are less carefully performed as can be seen from the fact that the areas corresponding to ornamental whitening and carbonate neoformations coincide.

Most samples of whitening and of carbonate neoformations from the perimeter of the settlements are represented in areas differing from those of concretionary formations of southern Oltenia, the Banat or southern Wallachia, thus confirming *the derivation from local sources of the ornamental whitening on the Middle Neolithic earthenware from Vădastra and Crușovu.*

#### The manufacture of ornamental whitening

The proportion of the various mineralogic components in the carbonate neoformations can be considerably modified during the weathering processes by the percolation of carbonates and the

migration of hydrated oxides of iron, manganese, and aluminium. New horizons can thus be formed, with various shades of white, as the carbonate neoformations include a larger or smaller amount of clay minerals or of oxides of iron, manganese, etc.

The granules embedded in the ceramic mass have both the aspect and the chemical and mineralogic composition of the concretionary materials found in the carbonate accumulation horizons in the soils of the Vădastra site. The variation in the composition of the granules on one sherd (Table 2) is comparable to that existing in some concretions of the carbonate accumulation horizon.

Table 2

Composition of the granules embedded on the same fragment of pottery compared with the composition of two samples taken from the same concretionary fragment

Nr. of sample	Analysed sample	Ca (%)	Mg (%)	Fe (%)	Sr (ppm)
293	Whiting, meander decoration	21.2	0.60	1.22	281
294	Whiting, spiral decoration	23.4	0.79	1.02	312
1515	Carbonate concretions	22.1	0.89	1.44	327
1516	Carbonate concretions	24.7	0.91	1.21	280

The incrustations of white paste exhibit a much more homogeneous composition and generally have a higher content of calcium carbonate (Table 3). In such cases, variations in composition are also smaller.

Table 3

Composition of the incrustations of white paste on the same fragments Vădastra II pottery from Vădastra

Nr. of sample	Analysed sample	Ca (%)	Mg (%)	Fe (%)	Sr (ppm)
167	Whiting-vessel double spiral	31.55	0.53	0.74	396
168	Whiting-vessel double spiral	31.12	0.57	0.68	388
311	Whiting-vessel with lozenge design	28.90	0.77	0.91	402
312	Whiting-vessel with lozenge design	28.62	0.69	0.89	397

The conspicuous differences between the two types of ornamental whiting suggest that the encrusted paste might be a white material obtained by processing some concretionary materials. Moreover, as was shown for the samples of ornamental whiting and the concretionary sources at Vădastra and Crușovu (Table 1), the concretionary material contains more quartz and less calcite than the whiting on the Vădastra II pottery from Vădastra and Crușovu. The finer texture and the degree of homogeneity of the samples of ornamental white paste from the same sherd denote a processing by means of wet treatment of the carbonate concretionary forms.

All these considerations lead to the conclusion that the processing of the concretionary materials might have included their grinding followed by mixing with water to a kind of barbotine from which were removed the suspensions of clay minerals and iron oxides as well as the coarse material containing quartz granules of sizes comparable with the sand fraction. In this way, the paste is enriched in calcium carbonate and the whiteness of the material is improved. Calcium carbonate is obviously the determinant factor of ornamental whitening; quartz and, contingently, dolomite maintain this colour while organic matter, hydrated iron and manganese oxides, or clay minerals, are detrimental to whiteness. Hydrochloric acid (1/3) decomposes the carbonates and solubilizes calcium, strontium and magnesium but also reacts with iron oxides and clay minerals so that cations from these minerals enter the solution.

It may be accepted in a first approximation that the intensity of whiteness of the ornamental whitening can be appraised by the amounts of calcium and iron in the hydrochloric extract, or by the Ca/Fe ratio of these two cations. As a matter of fact, the experimental points in calcium/iron diagram corresponding to the samples of whitening and to the carbonate neoformations generally lie in a band centered along a straight line  $y=40-16.2x$  (fig. 16). A relatively small field contains the points corresponding to the Vădastra ornamental whitening, together with concretionary forms from the area of the settlement. The field of the neoformations and of the carbonate deposits on sherds of pottery in the Vădastra soil is wider in the region of lower calcium concentrations. The points corresponding to the whitening on pottery of Vădastra I phase and on figurines and vessels of Vădastra II phase are not grouped separately but are scattered together on the entire field, an indication that the whitening used for pottery and for the figurines was the same. The positions of the areas of the samples from Vădastra show that some of the concretionary forms might have been used directly, while others were processed in order to enrich them in calcium, i.e. in calcium carbonate, by eliminating the minerals which give off iron, such as hydrated iron oxides, clay minerals, etc.

The ornamental whitening on earthenware of phases Vădastra I and II at Crușovu corresponds to a much wider field than that of the Middle Neolithic whitening of Vădastra, a field containing nearly all the points corresponding to the concretions and carbonate deposits. This coincidence of the field of the ornamental whitening with that of the neoformations within the settlement indicates a less advanced technology in the selection and processing of the sources of whitening or a less abundant occurrence of carbonate

- Ornamental whitening:
  - Vădastra I-Vădastra,
  - pottery and
  - ⊙ figurines Vădastra II-Vădastra,
  - △ Vădastra I and
  - ▲ Vădastra II-Crușovu,
  - ▼ Vădastra II-Celeiu.
- Carbonate deposits on sherds belonging to the Vădastra culture:
  - × Vădastra,
  - △ Crușovu,
  - ▽ Celeiu.
- Carbonate concretions:
  - + Vădastra,
  - ∨ Crușovu,
  - ⊖ not utilized sources of whitening at Vădastra.

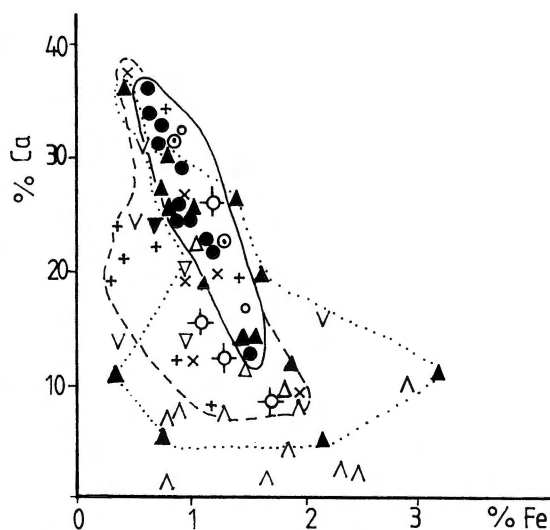


Fig. 16. Distribution of the samples of ornamental whitening, of carbonate neoformations and of some not utilized sources of whitening in regard to their contents in calcium and iron.

neoformations, these also having wide variations of composition. *The samples of whitening from Celeiu and Hoțărani are grouped in the vicinity of the points corresponding to the concretionary forms gathered within the perimeter of these settlements.*

The increased density of the points corresponding to the ornamental whitening with increasing calcium and diminishing iron content rather suggests a processing of local concretionary sources, the points corresponding to the neoformations having a higher density below the 26 % Ca content. The degree of whiteness may be expressed numerically by the Ca/Fe ratio; the higher the amount of calcium carbonate, the higher will be the intensity of whiteness, while with increasing iron content, the material loses its whiteness and acquires more and more brownish or reddish shades.

In a diagram presenting the concentration of calcium carbonate plotted against the Ca/Fe ratio (fig. 17), the ornamental whitening and the carbonate neoformations from Vădastra fall within a more restricted area than that corresponding to the Crușovu samples. The smaller variation in the composition of the Vădastra samples can be ascribed to the abundance and the lesser variation of the utilized sources, such as those cropping up in the banks of the Obîrșia brook near the Vădastra settlement as compared with the carbonate concretions in the lithological strata at Crușovu.

Most of the points corresponding to samples of whitening and carbonate concretions from within the investigated Middle Neolithic settlements appear along an ascendant curve which shows that the degree of whiteness expressed by the Ca/Fe ratio increases together with the quantity of calcium carbonate. Are an exception a group of five dolomite-containing concretionary forms from Vădastra and a group of three samples of ornamental whitening from Crușovu. These exceptions may be explained by the presence in these samples of components, such as quartz, which contribute to whiteness.

A diagram of the variation of the Ca/Fe ratio in terms of the amount of quartz present in the analysed samples show the representative points scattered almost over the entire field of the diagram (fig. 18). Significantly, the points corresponding to ornamental whitening on earthenware from Vădastra are gathered within a restricted area between 24-44 % SiO<sub>2</sub>, confirming a selection of the concretionary material

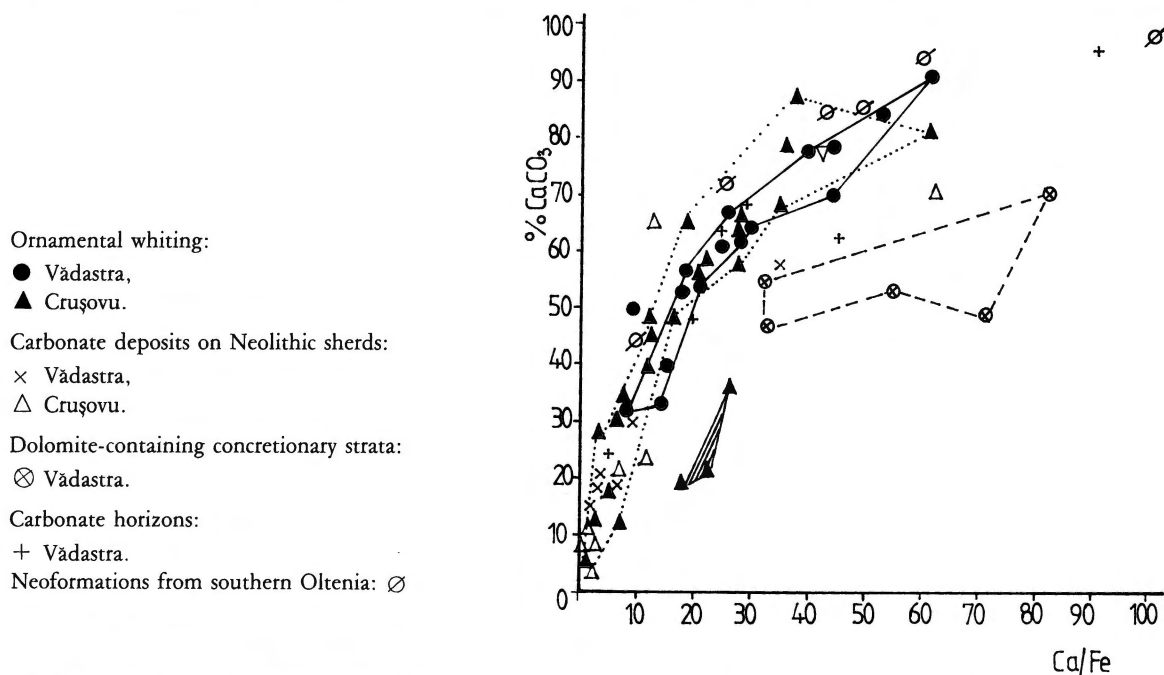


Fig. 17. Distribution of the samples of whitening, of the carbonate neoformations and of some neoformations from southern Oltenia in regard to their contents in calcium carbonate and their Ca/Fe ratio.

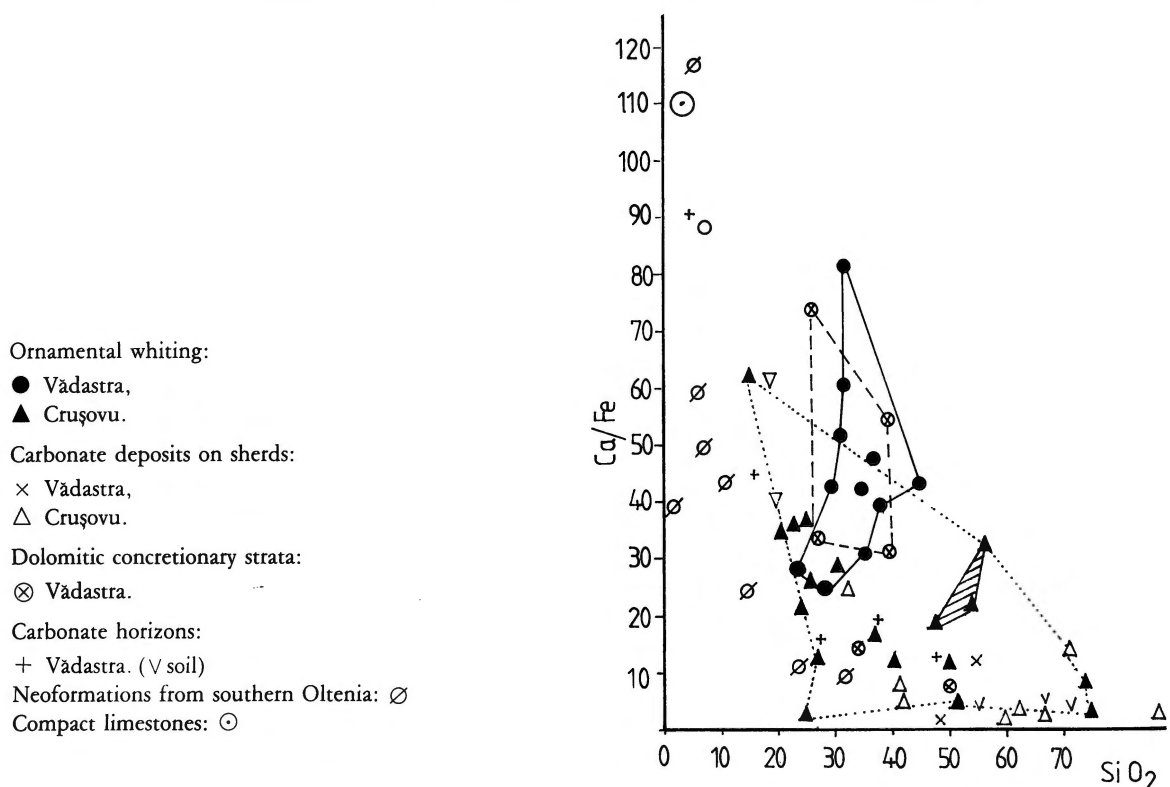


Fig. 18. Distribution of the samples of whitening and of the carbonate neoformations in regard to their Ca/Fe ratio and their quartz contents.

aiming to improve whiteness. The samples of dolomite-containing neoformations from Vădastra, which were grouped separately in fig. 17, are here superimposed over the field of the whitening from Vădastra; nevertheless, probably owing to the presence of coarse sand, these materials were not utilized as such for ornamental whitening<sup>17</sup>.

The points corresponding to the ornamental whitening on the Vădastra culture earthenware at Crușovu cover a wide field in which quartz attains concentrations of up to 75 %. The three samples of whitening in fig. 17 are met again in this diagram at SiO<sub>2</sub> concentrations of 48 to 56 %, corroborating the deviation observed in this figure, caused by their high quartz content. The marked dispersion of the points in this diagram shows that the participation of quartz as a dominant mineral in the whitening is comparatively small, this mineral being only a diluting agent which does not impair the whiteness due to calcium carbonate. The close clustering of the points corresponding to the ornamental whitening of pottery from Vădastra attests *the selection and processing of local concretionary materials, for ornamental whitening*. At Crușovu, the preparation technology of the ornamental whitening is not evident, the representative points for ornamental whitening and for the local carbonate neoformations being interspersed with each other all over the field.

The sorting and processing of the local concretionary carbonate materials for obtaining the whitening used on the clay objects was demonstrated by:

- The higher content of calcium carbonate in the ornamental whitening.

<sup>17</sup> Dolomite-containing neoformations also have from 2 – 18 % coarse sand.

- The smaller fields of incidence in the Ca-Fe, CaCO<sub>3</sub>-Ca/Fe and Ca/Fe-SiO<sub>2</sub> diagrams for the clay objects dug up at Vădastra as compared to the field corresponding to the sources.
- The higher Ca/Fe ratio in the ornamental whitening than in local carbonate neoformations.
- The higher degree of homogeneity in the make-up of the ornamental whitening than in local carbonate neoformations.

#### The technique of applying the decoration on the earthenware of the Vădastra culture

The whitening was spread on the surface of the air-dried clay objects by means of some kind of brush, as can be inferred from the traces sometimes visible in the paste. The layer of whitening applied on the unfired surfaces incorporated in the paste some material from the ground, thus lessening its carbonate content. This explains why the applied whitening contains 20–25 % CaCO<sub>3</sub> but over 40–50 % SiO<sub>2</sub>. Such concentrations are found, within similar intervals, in the whitening applied on earthenware of the Starčevo-Criș, Vădastra, Boian cultures, an evidence of the continuity of this technique throughout the Middle Neolithic along the Lower Danube.

The whitening was certainly applied in successive layers until the desired degree of whiteness was reached. The taking of four successive samples from the surface downwards, from a thicker application on the foot of a vessel of Vădastra II phase from Vădastra discovered in the 1974 diggings and the analysis of the four samples together with the analysis of the ceramic mass by absorption in infrared light (fig. 19) revealed a variation of the composition from the surface towards the wall of the vessel. With increasing depth, the calcite content decreases while the quartz content increases. This variation in the content of predominant minerals can only result from the whitening being applied on the unfired ceramic mass which, under the influence of the moisture in the carbonate suspension, penetrates the layer of whitening. This also explains *the good adhesion of the whitening on the walls of the earthenware*. Encrusting with whitening in the incisions was performed after the object was dried at ambient temperature.

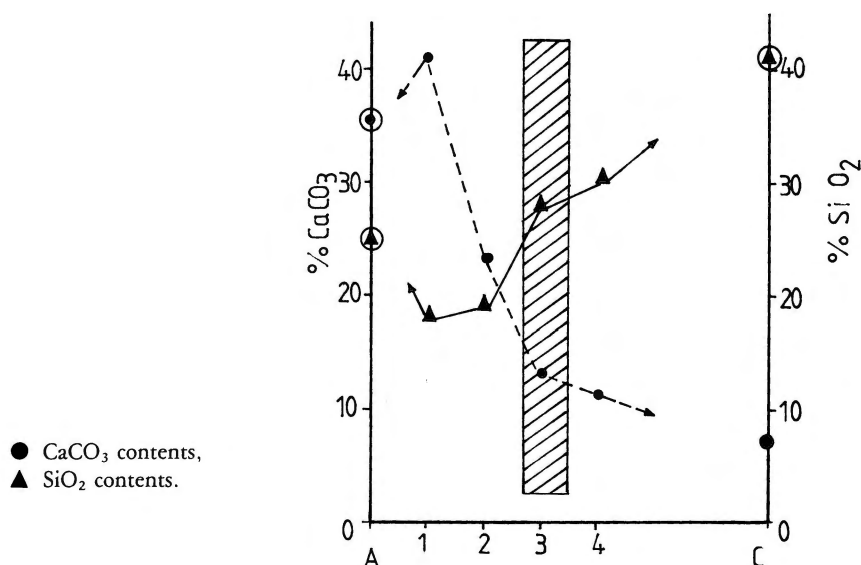


Fig. 19. Variation of the calcium carbonate and quartz contents plotted against the depth of sampling in the white coating on the leg of a Vădastra II vessel from Vădastra, 1974 (analyses by absorption in infrared light).

### The firing of the Vădastra pottery

After being decorated, the ware was fired in pits<sup>18</sup> with direct flame and reducing atmosphere. This technological scheme is supported by the following features of the Vădastra II earthenware from Vădastra:

- The very conformity to shape and adherence of the ornamental whitening to the surface of the clay objects.

- The coincidence between the firing temperatures of the ornamental white and of the ceramic mass, as results from the concomitant presence or absence of kaolinite in the whitening and the paste of the Vădastra II phase earthenware from Vădastra and Cruşovu.

- The higher content in zinc, copper and lead in the ornamental whitening than in the concretionary material in the Vădastra settlement.

As a matter of fact, with earthenware is fired in direct contact with the flame, the smoke deposits fine carbon particles on the surface and in the pores of the objects, together with microelements from the straw and wood used as fuel (Table 4).

Table 4

The content in microelements (ppm) of some samples of ornamental and concretionary materials from Vădastra

Nr.	Sample	Zn	Pb	Cu
130	Carbonate concretions	2.4	2.2	5.1
1425	Concretionary layer	4.8	3.4	8.8
307	Whiting from a Vădastra II grey vessel	19.1	6.6	11.2
394	Whiting from a Vădastra II black vessel	22.2	7.4	16.5

The analytical results of the ornamental whitening from the two vessels of the Vădastra II phase at Vădastra, when compared to the concretionary materials of the same site, make manifest a doubling of the copper and lead contents and a much greater increase in the zinc content of the ornamental whitening with respect to the microelements in the sources, as a result of selection and of firing in contact with the flame.

### Conclusions

- The whitening on the Vădastra culture earthenware as found at Vădastra and other similar settlements comes from local sources of carbonate neoformations.

- The likeness between the whitening found on sherds of the late Starčevo-Criş phases and of the Vădastra I and II phases attests the continuity of supply with the same types of whitening as well as continuity in the procedure of preparation and in the utilization of whitening for decoration.

- The results of chemical and mineralogical analyses of the whitening found on vessels and figurines show that no particular whitening was resorted to for decorating figurines.

<sup>18</sup> CORNELIU N. MATEESCU, Săpături arheologice la Vădastra. Materiale și Cercetări arheologice V, 1959, 68 – 69.

- The avoidance of using dolomite-containing carbonate accumulations for ornamental whitening at Vădastra shows that the concretionary materials were selected with a view to obtaining good whiteness.
- The higher homogeneity and higher calcium carbonate concentration of white incrustations as compared to concretions testify to the processing of the raw material for ornamental white paste.
- The adherence of the white paint to the vessels and figurines, the embedding of the granules and the coincidence of firing temperature of the white paint and the ceramic mass prove that the decoration was performed on the air-dried pieces which were fired only afterwards.
- The marked increase of the microelements in the applied whitening as compared with local concretionary materials show that firing was performed in pits, in direct contact with the flame and in the reducing atmosphere of incomplete combustion.